

Supporting Information for

m-Benziporphodimethene—a New Porphyrin Analogue Fluorescence
Zinc(II) Sensor

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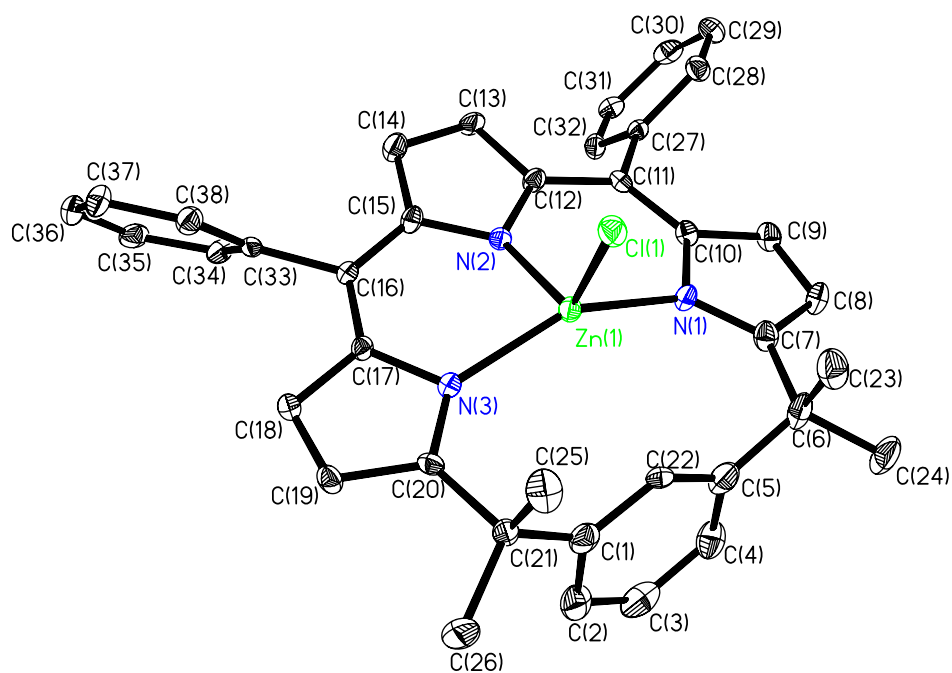
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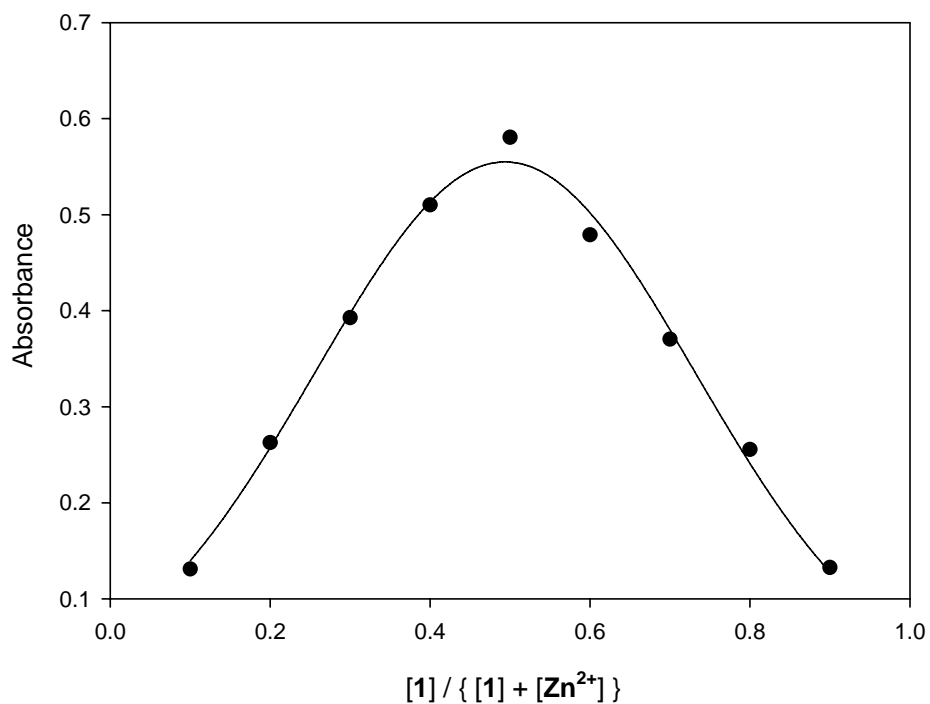
Synthesis of 1: A solution of α , α' -dihydroxy-1, 3-diisopropylbenzene (98 mg, 0.50 mmol), benzaldehyde (102 μ L, 1.01 mmol) and pyrrole (104 μ L, 1.51 mmol) in CH_2Cl_2 (150 mL) was treated with $\text{BF}_3 \cdot \text{OEt}_2$ (13 μ L, 0.10 mmol) and stirred at 27 $^\circ\text{C}$. Two hours later, DDQ (374 mg, 1.65 mmol) was added into the reaction mixture, and stirring was continued for two hours under 27 $^\circ\text{C}$. The reaction was quenched with triethylamine (10 drops) and then the solvent was removed in vacuum. The crude mixture was dissolved in minimum amount of CH_2Cl_2 and was purified by chromatography [SiO_2 (400 mL), eluted by CH_2Cl_2] to give **1** (72 mg, 0.136 mmole) [R_f = 0.11, CH_2Cl_2] in 27 % yield as a red powder.

^1H NMR (400MHz, CDCl_3 , 298K): δ = 1.75 (s, 12H; *meso*- CH_3), 6.19 (s, 2H; 13,14-H), 6.83 (*ab* quartet, $^3J(\text{H,H}) = 4.54$, 4H; 8,9,18,19-H), 7.29-7.48 (m, 13H; 2,3,4-H and *meso*-phenyl), 8.00 (s, 1H; 22-H), 12.46 (s, 1H; NH); ^{13}C NMR (400 MHz, CDCl_3 , 298K): δ = 29.17, 42.33, 121.50, 123.32, 125.12, 127.45, 127.78, 128.54, 129.06, 131.94, 136.83, 138.27, 138.46, 139.05, 147.38, 152.15, 182.20; UV-Vis (CH_3CN) [$\lambda_{\text{max}}/\text{nm}$ (log ϵ): 349 (4.56), 514 (4.28), 542 (4.31); Anal. Found (calc for $\text{C}_{38}\text{H}_{33}\text{N}_3 \cdot 0.5\text{C}_6\text{H}_{14}$): C 84.08 (85.67); H 7.32 (7.01); N 7.31 (7.31); HR-FAB-MS (m/z): calcd. $[\text{MH}]^+ = 532.2752$ obs. $[\text{MH}]^+ = 532.2745$

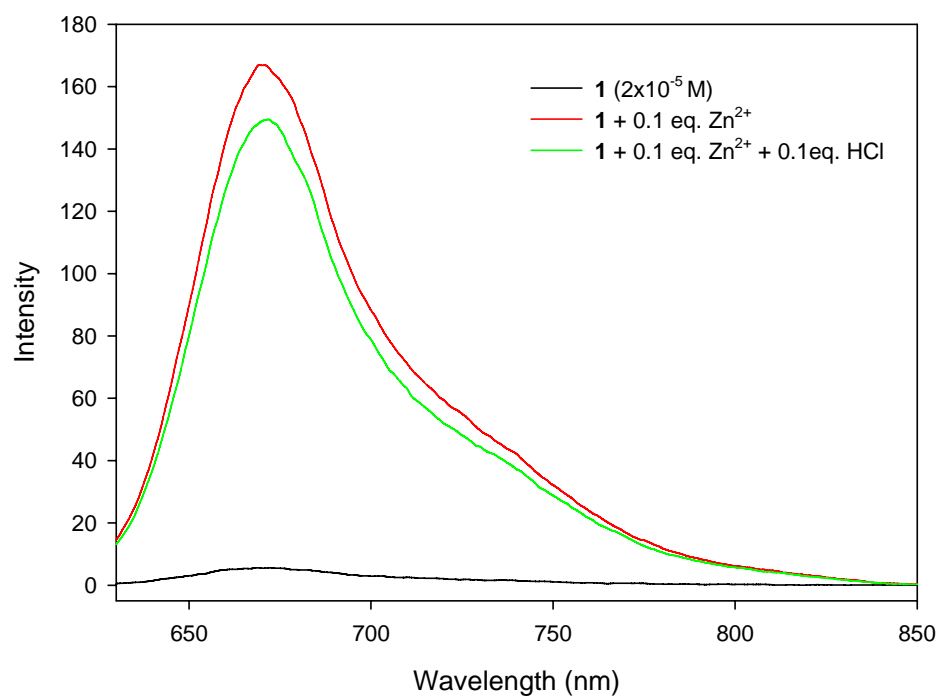
Synthesis of Zn•1: Anhydrous zinc chloride (51.3 mg, 0.376 mmol) was dissolved in CH_3CN , added into a solution of **1** (10 mg, 0.0188 mmol) in 30 mL $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:2), and added 1 drop of 2,6-lutidine into the solution. After two minutes of stirring, the solvent was removed under reduced pressure. Dried residue was dissolved in CH_2Cl_2 and excess zinc salt was extracted using distilled water. The organic layer was collected and solvent was removed in *vacuo*, and the dried product was dissolved in hexane. Slow evaporation of hexane yielded crystalline form of **Zn•1** (9.1 mg, 77 %). ^1H NMR (400 MHz, Acetone- d_6 , 298 K): δ = 1.97 (s, 6H; *meso*- CH_3), 2.14 (s, 6H; *meso*- CH_3), 6.05 (s, 2H; 13,14-H), 6.76 (d, $^3J(\text{H,H}) = 4.70$, 2H; 9,18-H), 6.98 (d, $^3J(\text{H,H}) = 4.70$, 2H; 8,19-H), 7.31-7.53(m, 13H; 2, 3, 4-H, *meso*-phenyl), 8.69(s,1H; 22-H); UV-Vis (CH_3CN) [$\lambda_{\text{max}}/\text{nm}$ (log ϵ): 350 (4.58), 593 (4.29), 639 (4.56); Anal. Found (calc for $\text{C}_{38}\text{H}_{32}\text{N}_3\text{ZnCl}$): C 71.38 (72.48); H 5.57 (5.13); N 5.85 (6.68); HR-FAB-MS (m/z): calcd. $[\text{M-Cl}]^+ = 594.1888$; obs. 594.1880.



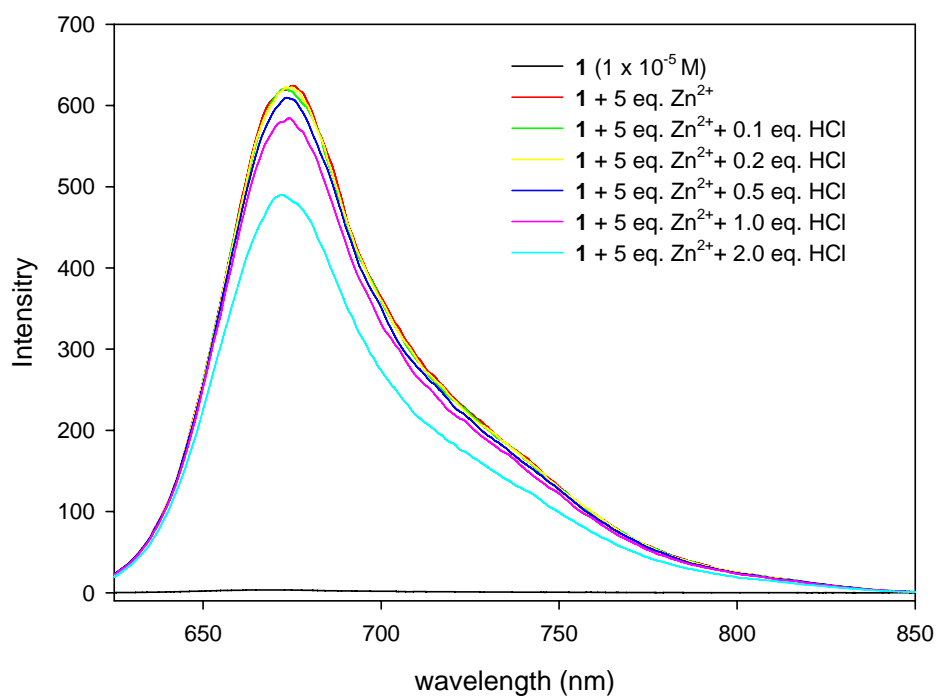
Supporting Figure 1. The ORTEP diagram of **1** in 30% probabilities of ellipsoids.



Supporting Figure 2. Job plot for the reaction of **1** with Zn^{2+} ion. Equimolar solutions (3.75×10^{-5} M) of **1** and Zn^{2+} (from $ZnCl_2$) in CH_3CN were prepared. To obtain the plot, **1** and Zn^{2+} solutions were mixed in various volume ratios (1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1). Neat 2,6-lutidine was added to each volume ratio to give a 0.014 M final concentration of 2,6-lutidine.



Supporting Figure 3. The fluorescence intensity changes when **1** (2×10^{-5} M) was treated with 0.1 equiv. of Zn^{2+} and then 0.1 equiv. of HCl.



Supporting Figure 4. The fluorescence intensity changes when **1** (1 x 10⁻⁵ M) was treated with 5 equiv. of Zn²⁺ and increasing amount of HCl.